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Selected ion flow drift tube studies of the reactions of $Si^+(^2P)$ with HCl, H_2O, H_2S, and NH_3: Reactions which produce atomic hydrogen

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The reaction rate coefficients, k, for the reactions of ground-state $Si^+(^2P)$ with HCl, H_2O, H_2S, and NH_3, have been measured as a function of reactant ion/reactant neutral center-of-mass kinetic energy, KE_{CM}, in a selected ion flow drift tube (SIFDT) apparatus, operated with helium at a temperature 298±2 K. The values k of the studied reactions have very pronounced, negative energy dependencies; the rate coefficients decrease by about 1 order of magnitude as KE_{CM} increase from near thermal values to ~2 eV. The results are interpreted in terms of a simple model assuming the reactions to proceed via the formation of long-lived complexes. These intermediate complexes decompose back to reactants or forward to products, the unimolecular decomposition rate coefficients for these reactions being k_1 and k_2, respectively. It is found that a power law of the form $k_{-1}/k_2=\text{const}(KE_{CM})^m$ closely describes each reaction. © *1995 American Institute of Physics.*

I. INTRODUCTION

A large number of reactions of the silicon ion Si^+ have been studied by Lampe and co-workers using a tandem mass spectrometer[1–6] (see also a review by Lampe[7] and references therein). A selected ion flow tube (SIFT) study on the reactions of Si^+ with H_2O, O_2, H_2, and NO (at 300 K) has been carried out by Ferguson *et al.*[8] Bohme, Wlodek, and co-workers have made systematic studies of the reactions of atomic $Si^+(^2P)$ ions focused on the kinetics, energetics, and the mechanism of these reactions leading to the chemical bonding of silicon with hydrogen, carbon, nitrogen, oxygen, and sulfur,[9–15] (see also reviews by Bohme[16,17] and references therein). These studies have been carried out using a selected ion flow tube (SIFT) apparatus at 298 K and a helium buffer gas pressure of 0.35 Torr. A guided ion beam apparatus has been used by Armentrout and his co-workers to study cross sections, mechanisms, and thermochemical aspects of several reactions of $Si^+(^2P)$ ions at kinetic energies ranging from thermal to ~10 eV[18–24] (see also reviews by Armentrout[25,26]). In a selected ion flow drift tube (SIFDT) study carried out by Fahey *et al.*,[27] the mobility of Si^+ in He has been measured, and the influence of the speed distribution of the Si^+ ions drifting in He on the measured reaction rate coefficients has been discussed.

Recently the structure, thermochemistry, and the reactions of many silicon-bearing ions with neutral molecules have been the subject of theoretical (see, e.g., Refs. 28–36) and various experimental studies (see, e.g., photoionization mass spectrometric studies,[37,38] a review by Bohme,[16] and references therein).

The reactions of atomic silicon ions are important for the chemistry of interstellar clouds,[39–42] and of the earth's ionosphere.[8] These reactions also could be of interest to the theoretical chemist because of fundamental aspects of the chemical bonding of atoms to silicon.

Charge transfer or dissociative charge transfer (e.g., fragmentation of hydrocarbons in reactions with ions of rare gases[43]) are essentially excluded when Si^+ ions, having a low recombination energy of only 8.15 eV are reacting at near thermal energies with any small molecules. The reactions usually proceed by incorporation of Si^+ into the molecular product ions (see compilation by Anicich[44] and reviews by Bohme[16,17]). This requires a rearrangement of existing bonds within the reactant molecule and the formation of new bonds. Such processes can take place only when a long lived intermediate complex is formed. The mechanism of such a reaction is reflected in its kinetics. They typically show pronounced energy dependencies of their reaction rate coefficients. In the case of association reactions the energy dependence of the reaction rate coefficient is rationalized as a consequence of the lifetime of the intermediate complex towards dissociation back to the reactants (see, e.g., discussion in Ref. 65). In the case of a binary reaction proceeding via formation of an intermediate complex the overall reaction rate coefficient can be rationalized in terms of the energy dependence of the lifetime of this complex against dissociation backward to reactants and forward to products.

In recent SIFDT studies in our laboratory we have studied a number of reactions, the reaction rate coefficients of which decrease strongly when KE_{CM} (indicating the reactant ion/reactant molecule average center-of-mass collisional energy) increases, starting from collisional limiting values at room temperature.[45–48] Also the presently reported reactions of Si^+ have similar dependencies on KE_{CM}. We will show that such reactions appear to proceed via the formation of long-lived complexes, the rate coefficient for the decomposition of which (back to reactants or forward to products) depends on the interaction energy in a power-law fashion.

The first step of any of the reactions studied, namely, the formation of the ion–molecule collision complex is limited by the capture rate coefficient k_C. The values k_C, for reactions of ions with nonpolar molecules are, according to simple Langevin theory, expected to be temperature independent $[k_{\mathrm{CL}}=2\pi e(\alpha/\mu_r)^{1/2}$, in c.g.s. units, where α is the polarizability of the neutral reactant molecule, μ_r is the reduced mass of the reactant ion/reactant neutral molecule, and e is the charge of the ion]. The slightly temperature dependent rate coefficients for reactions involving polar molecules are often calculated according to the ADO theory $[k_{C-\mathrm{ADO}}(T) = k_{\mathrm{CL}} + 2Ce\mu_d(2\pi/\mu_r k_B T)^{1/2}$, where μ_d is the permanent dipole moment of the reactant molecule, k_B is Boltzmann's constant, and C is a dipole locking constant which, at a given temperature, is a function of $(\mu_d/\alpha)^{1/2}$ only[49,50]]. A more recent approach to the calculation of collisional rate coefficients is done by using parametrization of the results of trajectory calculations due to Su and Chesnavich.[51] When collisional rate coefficients have to be calculated for temperatures below 300 K, an adiabatic capture theory (see review by Clary[52]) or statistical capture theories[53,54] are used. In all the following the capture rate coefficients are indicated by k_C, whether they represent Langevin limiting values, k_{CL}, or values calculated according to the above mentioned ADO theory or the more recent models of Su and Chesnavich.[51]

In drift tubes $\mathrm{KE_{CM}}$ can be increased to values up to a few eV where theories which predict thermal energy capture rate coefficients no longer apply. Reaction rate coefficients measured in drift tubes at elevated energies are often observed to exceed k_C calculated for 300 K. This phenomenon has been discussed in several recent papers[55] (see also discussion in Ref. 56), where the capture rate coefficient is predicted to increase as $T^{0.5}$ [i.e., as $(\mathrm{KE_{CM}})^{0.5}$] at suprathermal energies typical to those acquired in drift tube experiments. In a recent paper[47] we introduced an empirical correction function β (dependent only on $\mathrm{KE_{CM}}$) derived from many experimental data. This function is equal to unity at near thermal energy and increases with increasing $\mathrm{KE_{CM}}$, and has a value of approximately ~2 at $\mathrm{KE_{CM}}=2$ eV. We assume, that the actual capture rate coefficient $k_C = \beta k_{C_0}$, where k_{C_0} is the capture rate coefficient for a particular reaction at low $\mathrm{KE_{CM}}$ (limiting value for $\mathrm{KE_{CM}}$ approaching thermal energy). In Fig. 1 the correction factor β used for the present work is plotted and for demonstration experimental data $k_{\mathrm{exp}}/k_{0\mathrm{exp}}$ (equivalent to k_C/k_{C_0}, if a reaction is proceeding at the capture rate) as obtained for the fast reactions of C^+ with H_2S and C^+ with NH_3 are included. In the following, when energy dependencies of reactions are discussed, the term "capture rate coefficient, k_C" always refers to the value βk_{C_0}.

In order to describe the kinetics of the presently investigated ion–molecule reactions we consider that the reactions proceed via the formation of long-lived excited intermediate complexes which subsequently decompose back to reactants or forward to products. Thus the following reaction scheme is appropriate:

$$A^+ + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (AB^+)^* \xrightarrow{k_2} C^+ + D, \tag{1}$$

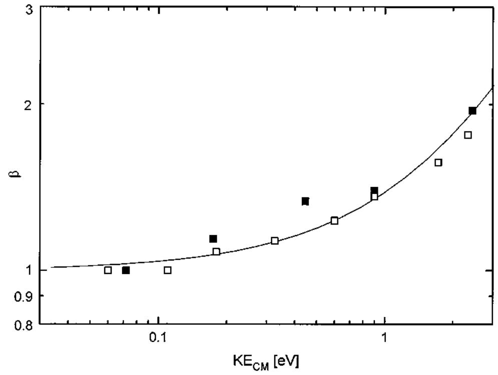

FIG. 1. The empirical correction factor β (solid line) obtained from the measured rate coefficients for the fast ion–molecule reactions (Ref. 47). β is the average value of $k(\mathrm{KE_{CM}})/k_0$, where k_0 is the limiting value of k for $\mathrm{KE_{CM}}$→thermal value. For demonstration $k(\mathrm{KE_{CM}})/k(\mathrm{KE_{CM}}=0.038$ eV) vs $\mathrm{KE_{CM}}$ for the reactions of C^+ with H_2S (symbol ■) and C^+ with NH_3 (symbol □), as were measured in present experiment, are also plotted.

where k_1 is the bimolecular rate coefficient for the formation of the excited intermediate complex $(AB^+)^*$, and k_{-1} and k_2 are unimolecular rate coefficients for dissociation of the excited intermediate complexes into the primary ion/neutral reactant and the product ion/product neutral, respectively. We assume that the excited intermediate complex is formed at the capture rate, k_C. Such an assumption is very common (e.g., in discussion of vibrational quenching by Ferguson[57]). We want to stress the fact, that in the following we use the specific values $k_1 = k_C = \beta \cdot k_{C_0}$. By applying simple reaction kinetics and using the steady-state approximation to $(AB^+)^*$, the following relationship is obtained for the overall rate coefficient k of reaction (1):

$$k = k_1 \frac{k_2}{k_{-1}+k_2} = \beta \cdot k_{C_0} \frac{1}{1+\dfrac{k_{-1}}{k_2}}. \tag{2}$$

From this relation it is evident that the ratio (k_{-1}/k_2) and its dependence on $\mathrm{KE_{CM}}$ is governing the energy dependence of the overall reaction rate coefficient k, as long as the assumption that the complex is formed at the capture rate is valid, and as long as the capture rate has only a weak or no dependence on $\mathrm{KE_{CM}}$. Note at this point that for the same conclusion (concerning dependence of k on k_{-1}/k_2) it will be sufficient to assume, that the rate of formation of an intermediate complex is nearly constant, but not necessarily equal to the capture rate coefficient.

On the basis of statistical arguments,[58] in analogy with the ideas widely discussed for three-body association reactions[59,60] and on the basis of our studies of many ion–molecule reactions proceeding via formation of long lived intermediate complexes,[45–48,61–63] we assume here that the ratio (k_{-1}/k_2) will vary with $\mathrm{KE_{CM}}$ in a power law fashion: $(k_{-1}/k_2) \propto (\mathrm{KE_{CM}})^m$. Expression (2) can then be rewritten as

$$k = \beta \cdot k_{C_0} \cdot \frac{1}{1+\left(\dfrac{\mathrm{KE_{CM}}}{\mathrm{KE_{CM1}}}\right)^m}, \tag{3}$$

where m and $\mathrm{KE_{CM1}}$ are constants ($\mathrm{KE_{CM1}}$ is the value of $\mathrm{KE_{CM}}$ at which k has decreased to 1/2 of its maximum value and hence for which $k_{-1}=k_2$). The parameters k_{C_0}, $\mathrm{KE_{CM1}}$, and m can be obtained from the fit of the experimental data.[46,47] In order to visualize the dependence of k_{-1}/k_2 on $\mathrm{KE_{CM}}$, k_{-1}/k_2 can be expressed explicitly by using formulas (2) and (3) as

$$\frac{k_{-1}}{k_2}=\left(\frac{\beta k_{C_0}}{k}-1\right)=\left(\frac{\mathrm{KE_{CM}}}{\mathrm{KE_{CM1}}}\right)^m. \tag{4}$$

Using the measured values $k(\mathrm{KE_{CM}})$, the function $\log(\beta(k_{C_0}/k)-1)$ vs $\log(\mathrm{KE_{CM}})$ can be plotted. If $(\mathrm{KE_{CM}}/\mathrm{KE_{CM1}})\gg 1$, then Eq. (3) can be written in form

$$k\doteq\beta\cdot k_{C0}\cdot\left(\frac{\mathrm{KE_{CM}}}{\mathrm{KE_{CM1}}}\right)^{-m}. \tag{5}$$

This form of the dependence of a rate coefficient on energy (temperature) has been observed many times for three-body association reactions (e.g., Refs. 64–68) where the value of m was coupled to the number of rotational degrees of freedom in the reactants and products. We will use the parameter m to characterize the energy dependencies of the studied reactions.

II. EXPERIMENT

The experiments were performed using the Innsbruck selected ion flow drift tube (SIFDT) of conventional design.[69,70] The reactant ions Si$^+$ were produced from SiH$_4$ in a high pressure electron-impact ion source, Ar was added to the ion source in order to enhance the production of Si$^+$ ions and to decrease the contamination of the ion source caused by the presence of SiH$_4$. The ions were subsequently mass selected in a quadrupole mass filter and injected into the flow tube via a venturi-type inlet. In the upstream part of the drift tube, prior to the reaction region, low E/N was used (E is the electric field strength in this part of the drift tube and N is the buffer/carrier gas number density). In this "thermalization" part of the drift tube the average collision energy of the ions with the buffer gas atoms was kept below 0.1 eV.

The reactant and product ions were monitored downstream with a second quadrupole mass filter as a function of the flow rate of the added neutral reactant. Established methods of analysis were used to derive reaction rate constants and product distributions.[71,72]

In order to determine the internal state of the Si$^+$ ions in the reaction region of the drift tube in the present experiment, D$_2$ was added as a reactant gas. No production of SiD$^+$ or any other reaction of Si$^+$ with D$_2$ was observed. It is known[10,26] that the reaction of the ground-state Si$^+$(^{2}P) with D$_2$ is endoergic and very slow ($<2\times10^{-13}$ cm^3 s^{-1}) whereas the reaction of the excited state Si$^{+}*$ (probably ^{4}P state) with D$_2$ is fast (7.7×10^{-10} cm^3 s^{-1}) yielding the product SiD$^+$. We therefore concluded that the Si$^+$ ions are in their ground-state Si$^+$(^{2}P) in the present experiment.

$\mathrm{KE_{CM}}$ was derived by means of the Wannier expression.[73] The mobility of Si$^+$ ions in He was measured in the present experiment and it agrees well with the mobility data obtained by Fahey *et al.*[27] The accuracy of the measured rate coefficients is assumed to be ±30% as is usual for swarm experiments of the SIFDT type.

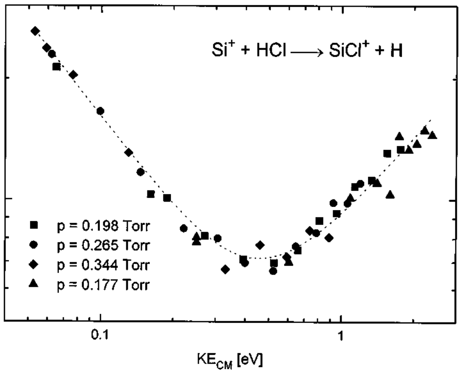

FIG. 2. The variation of the reaction rate coefficient with $\mathrm{KE_{CM}}$ for the reaction of Si$^+$(^{2}P) with HCl ($k_{\mathrm{CL}}=9.56\times10^{-10}$ cm^3 s^{-1}). Different buffer gas pressures are indicated by different symbols.

III. RESULTS AND DISCUSSION

The reaction rate coefficients and product ion distributions were determined for the reactions of Si$^+$(^{2}P) ions with the small 2, 3, and 4 atoms containing inorganic molecules HCl, H$_2$O, H$_2$S, and NH$_3$ over the energy range of $\mathrm{KE_{CM}}$ from thermal (≈0.04 eV) to about 2 eV. All these reactions are fast (with rate coefficients of a few times 10^{-10} to 10^{-9} cm^3 s^{-1}) at near thermal energies and their rate coefficients have a very pronounced negative energy dependence. The main neutral product in all these reactions is atomic hydrogen. We estimated standard reaction entropies for all the studied reactions and it is worth noting that mainly because of the production of H in these reactions, the standard reaction entropies in the studied reactions are all negative.

A. The reaction of Si$^+$(^{2}P) with HCl

The energy dependence of the reaction rate coefficient, k, of the title reaction

$$\mathrm{Si^+ + HCl \rightarrow SiCl^+ + H} \tag{6}$$

is shown in Fig. 2. To our knowledge there exists no previous study of this reaction. The values of k have a minimum at $\mathrm{KE_{CM}}\doteq 0.4$ eV. SiCl$^+$ was the only observed product ion over the whole $\mathrm{KE_{CM}}$ range covered. A possible association product SiClH$^+$ was observed only in traces (<0.5% of the total ion signal) and we did not observe any pressure dependence of the measured rate coefficients for helium buffer gas pressures ranging from 0.177 to 0.344 Torr. Before further treatment of the data, the measured rate coefficients were divided by the factor $\beta(\mathrm{KE_{CM}})$, as has been discussed in the Introduction. In the following, we will use the upper index β in k^β to indicate "β corrected" rate coefficients. The obtained $k^\beta=k/\beta$ is plotted vs $\mathrm{KE_{CM}}$ in a log–log plot in Fig. 3. We assume that two different reaction mechanisms are involved at low and high energies $\mathrm{KE_{CM}}$, respectively. Indexes I and II will be used to indicate the low and high energy processes, respectively. The low energy segment of the dependence of k^β on $\mathrm{KE_{CM}}$ is of the form $(\mathrm{KE_{CM}})^{-m}$ and we assume that at high-energy the dependence on $\mathrm{KE_{CM}}$ is of

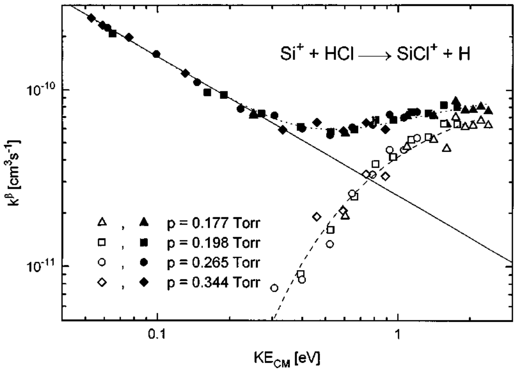

FIG. 3. The variation of the β corrected reaction rate coefficient, k^β, with KE_{CM} for reaction of $Si^+(^2P)$ with HCl (solid symbols). Straight solid line represents the best fit through the data in low energy region. The open symbols correspond to reaction rate coefficient, k_{II}, of the high energy process obtained by substraction of the reaction rate coefficient, k_I, of the low energy process from k^β, $k_{II}=k^\beta-k_I$ (see the text). Dashed line corresponds to the best fit through the data in Arrhenius plot in Fig. 4. Dotted line is the best fit curve according to Eq. (1). Different buffer gas pressures are indicated by different symbols.

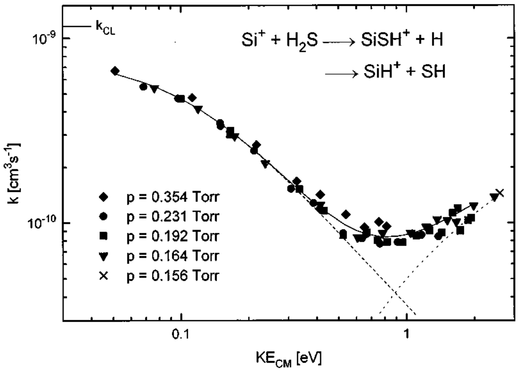

FIG. 5. The variation of the reaction rate coefficient k with KE_{CM} for the reaction of $Si^+(^2P)$ ions with H_2S. Different buffer gas pressures are indicated by different symbols. Dotted line corresponds to the best fit of the high energy segment of the data by function $\beta \cdot A \cdot \exp(-\frac{3}{2}E_a/KE_{CM})$, where $E_a=0.74$ eV is given by endoergicity of the channel (8b) of the reaction. By multiplication of the Arrhenius function by β, the β correction is taken into account. Dashed line corresponds to $\beta\, k_I$, where k_I characterize low energy segment of the data and is determined by the fit of the data in Fig. 7. The best fit of the data according to Eq. (7) after inverse β correction is indicated by solid line.

an Arrhenius type, involving an activation energy, E_a. Over the whole energy range covered k^β can be approximated by the expression

$$k^\beta = k_I + k_{II} = k_{I_0}(KE_{CM})^{-m} + k_{II_0} \exp\left(-\frac{E_a}{\frac{2}{3} KE_{CM}} \right), \tag{7}$$

where k_{I_0} is a "proportionality constant" and k_{II_0} is the "limiting value" of k^β at high KE_{CM}. In order to calculate the second term, k_{II}, in Eq. (7) representing the Arrhenius dependence, k_{II} was expressed as $k_{II}=k^\beta-k_I$ [k_I was extrapolated for that purpose from the low energy region by a straight (solid) line as shown in Fig. 3]. The calculated values k_{II} are plotted in Fig. 3 (open symbols). Figure 4 shows the Arrhenius plot of k_{II} vs $1/KE_{CM}$. From the Arrhenius plot in Fig. 4 an activation energy $E_a=0.7$ eV was calculated. The apparent linear fit through the data in the Arrhenius plot (Fig. 4) is indicated by a dashed line in Fig. 3. When using parameters $k_{I_0} = 0.8 \times 10^{-9}$ cm^3 s^{-1}, $m=1$, $k_{II_0} = 1.0 \times 10^{-10}$ cm^3 s^{-1}, and $E_a=0.7$ eV, obtained by a fit of both the low and high energy sections, we obtain a fit of k^β (dotted line in Fig. 3) and k (dotted line in Fig. 2), which are in good agreement with the data. Function (7) also was used earlier to fit the data of our previous studies,[46,47,61,62] on reactions of several small hydrocarbon ions with HCl, N_2O, CO_2, NH_3 and the ones of Viggiano *et al.*[74] on the reaction of $Kr^+(^2P_{3/2})$ with HCl and the obtained parameters m were discussed on the basis of internal degrees of freedom of the reactants.

To our knowledge the heat of formation of $SiCl^+$ is not known, but from the fact that the reaction (6) is fast at low KE_{CM} we assume that the reaction is exoergic or at least thermoneutral. Using values $\Delta H_f(Si^+)=295.8$ kcal/mol, $\Delta H_f(HCl)=-22.02$ kcal/mol, and $\Delta H_f(H)=52.095$ kcal/mol[75] we obtain an upper limit $\Delta H_f(SiCl^+) \lesssim 221.7$ kcal/mol.

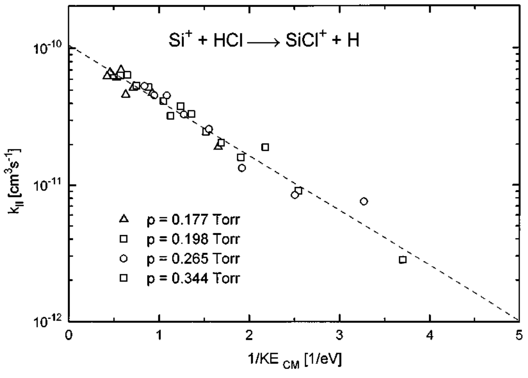

FIG. 4. Arrhenius plot of the reaction rate coefficient k_{II} corresponding to the high energy process of the reaction of $Si^+(^2P)$ with HCl. Obtained Arrhenius activation energy $E_a=0.7$ eV. Dashed line is the best apparent linear fit. Different buffer gas pressures are indicated by different symbols.

B. Reaction of $Si^+(^2P)$ with H_2S

The energy dependence of the rate coefficient, k, for the reaction

$$Si^+ + H_2S \rightarrow (SiSH)^+ + H \tag{8a}$$

$$\rightarrow SiH^+ + SH \tag{8b}$$

is shown in Fig. 5. This reaction was used by Fox *et al.*[13] to produce ($SiSH^+$), which then was used as a reactant ion for further investigations, nevertheless the rate coefficient of reaction (8) was not reported. The rate coefficient obtained is independent of the pressure of the buffer gas and only traces of adduct, $SiSH_2^+$ ions, created by association reactions, were observed. The channel (8a) is exoergic, channel (8b) is endoergic by 0.74 eV (see Table I). The productions of both isomers, the more energetic $SSiH^+$ and the less energetic $SiSH^+$ ions are exoergic and may therefore occur (see dis-

TABLE I. Summarized data for the reactions included in this study. The reaction energetics are indicated as $\Delta E(=-\Delta H)$, calculated using the thermochemical data given in Refs. 10, 13, 24, and 75. The values for the rate coefficients are given in units of 10^{-9} $cm^3\ s^{-1}$ and energies ΔE and KE_{CM1} in eV.

Reaction	Product ion	Product neutral	ΔE	k_{CL}	k_{10}	k_{10}/k_{CL}	m	KE_{CM1}
Si^++HCl	$SiCl^+$	H		0.96	[a]		1.0	[a]
Si^++H_2S	$SiSH^+$	H	0.78±0.2	1.16	0.79	0.68	1.6	0.12
	$HSiS^+$	H	0.25±0.2					
	SiH^+ [b]	SH	−0.74					
Si^++H_2O	$SiOH^+$	H	1.4±0.2	0.85	0.29	0.34	2.9	0.104
	$HSiO^+$	H	−1.2±0.2					
Si^++NH_3	$SiNH_2^+$	H	0.74	1.07	0.77	0.72	2.0	0.13
	HSiNH	H	−1.56					

[a] For reaction of Si^+ with HCl low energy limit was not yet reached at the near thermal energies accessible in the present experiment.

[b] The product observed for energies above ~0.8 eV.

cussion in Ref. 13) in parallel. We did not determine which isomer actually is produced in the reaction. $(SiSH)^+$ is the dominant product at low KE_{CM}. The signal of SiH^+ is increasing at elevated KE_{CM} and is becoming the dominant product above 0.8 eV. We cannot show the actual product distribution because the masses of the product ions differ by a factor of 2 and thus the mass discrimination of the quadrupole system may be substantial. The obtained relative product distribution is in qualitative agreement with the obtained values k_I and k_{II} as discussed below. As shown for the reaction of Si^+ with HCl, also here the rate coefficient k^β for the overall reaction can be written in the form: $k^\beta=k_I+k_{II}$, where k_I and k_{II} correspond to the channels (8a) and (8b), respectively. We assume that the energy dependence of the rate coefficient k_{II} of the endoergic channel (8b) has an Arrhenius form with an activation energy equal to the endoergicity of the reaction, $E_a=0.74$ eV. Therefore, the high energy segment of the data was fitted by the function $\beta\cdot A\cdot\exp(-(3/2)E_a/KE_{CM})$ with $E_a=0.74$ eV, and the parameter A was determined as shown by the dotted line in Fig. 5. In the low energy region the endoergic channel (k_{II}) is negligible and $k_I\doteq k^\beta$. In the energy region where both processes (channels) overlap k_I has been calculated by subtraction of k_{II} from the experimental data, $k_I=k^\beta-k_{II}$. The obtained values k_I are shown in Fig. 6.

In order to visualize the form of the dependence of k_I on KE_{CM}, $((k_{I_0}/k_I)-1)$ vs KE_{CM} is plotted in Fig. 7. The excellent linearity of the plot $k_{-1}/k_2\propto(KE_{CM})^m$ justifies our assumption that two parallel reaction channels occur, the exoergic one (8a) resulting in the production $SiSH^+$ and the endoergic one (8b) producing SiH^+, predominantly at energies $KE_{CM}\geqslant 0.8$ eV. Parameters of the fit are listed in Table I.

C. The reaction of $Si^+(^2P)$ with H_2O

The reaction

$$Si^++H_2O\rightarrow SiOH^++H \tag{9}$$

has been studied only over the limited energy range, from thermal up to 0.3 eV. At higher energies the flow of the H_2O vapor was too small to obtain a sufficiently strong decay of the Si^+ signal allowing for an accurate calculation of the rate coefficient of the reaction. The energy dependence of the obtained rate coefficient is shown in Fig. 8. Thermal SIFT data of Fahey *et al.*[27] and Wlodek *et al.*[10] are included, and show very good agreement with the present data (low energy limit). Note that at thermal energy the measured rate coefficient of reaction (9) is only 1/4 of the capture rate coefficient, $k_{CL}\doteq 8.5\times10^{-10}$ $cm^3\ s^{-1}$. This observation disagrees with a

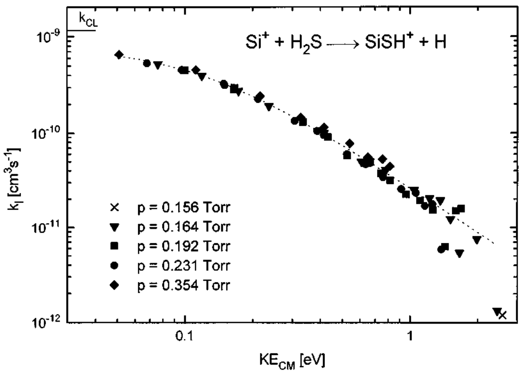

FIG. 6. The reaction rate coefficient, k_I, corresponding to the low energy process of the reaction of $Si^+(^2P)$ with H_2S, $k_I=k^\beta-k_{II}$, where k_{II} is the reaction rate coefficient corresponding to the endoergic production of SiH^+, obtained by fit of the high energy segment of the data (see text). Dotted line corresponds to straight line in Fig. 7. Different buffer gas pressures are indicated by different symbols.

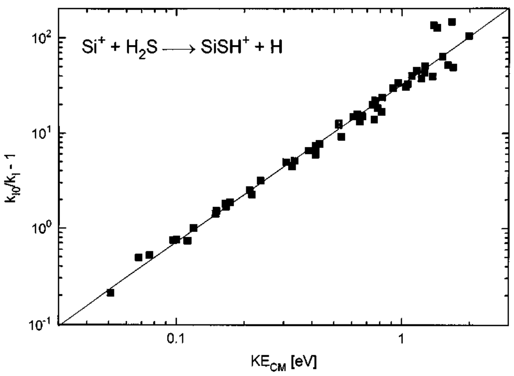

FIG. 7. Dependence of (k_{I0}/k_I-1) vs KE_{CM} of the data plotted in Fig. 6. Straight solid line is the best apparent linear fit of the data.

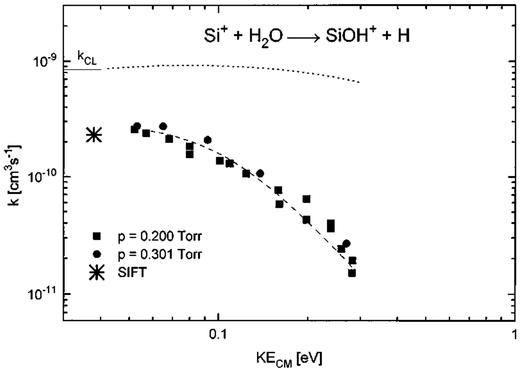

FIG. 8. The variation of the reaction rate coefficient with KE_{CM} for the reaction of $Si^+(^2P)$ with H_2O. * indicates SIFT data (Refs. 8, 10, 27). Dotted line represents the data obtained by calculation of the reaction rate coefficient from reported reaction cross section obtained in guided beam study (Ref. 21). Dashed line corresponds to straight line fit in Fig. 9. Different pressures are indicated by different symbols.

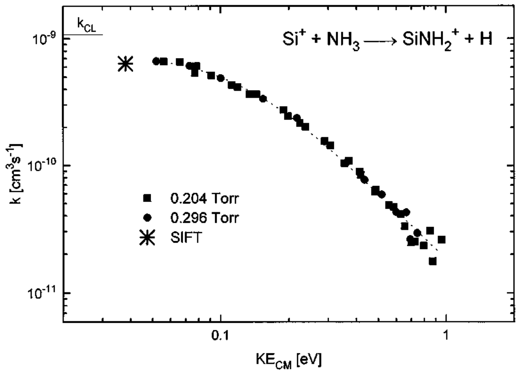

FIG. 10. The KE_{CM} dependence of the reaction rate coefficient of the reaction of $Si^+(^2P)$ with NH_3. * indicates SIFT data of Wlodek *et al.* (Ref. 77). Dotted line corresponds to best fit in Fig. 11. Different pressures are indicated by different symbols.

guided ion beam study of this reaction,[21] where cross sections equal to the collisional cross section have been reported for energies from 0.02 up to 0.2 eV. Also the reported relative change of the cross section of the reaction (9) as dependent on the collision energy is not in agreement with the energy dependence of the reaction rate coefficients obtained in the present study (dotted line in Fig. 8 represents the reaction rate coefficients as calculated from the cross sections reported in Ref. 21). There exist two isomers $SiOH^+$ and $HSiO^+$, but while the production of $SiOH^+$ in the reaction of Si^+ with H_2O is exoergic by 1.4 eV, the production of the $HSiO^+$ isomer is endoergic by 1.2 eV (see Table I). Thus in the present study the product ion can only be the $SiOH^+$ isomer (see also discussion by Bohme[76]). The obtained energy dependence of the reaction rate coefficient (plot in Fig. 8) has a form similar to the low energy parts (k_I) of the dependencies of the rate coefficients for the reactions of Si^+ with HCl and H_2S. Therefore Eq. (3) was used to fit the data in Fig. 8, and the obtained fit is represented by a dashed line. The obtained parameters of the fit are listed in Table I. Figure 9 shows the log–log plot of the function $((\beta\cdot k_0)/(k)-1)$ vs KE_{CM} as discussed in Sec. I. Because KE_{CM} did not exceed 0.3 eV, $\beta \doteq 1$, and the "β correction" is negligible.

D. The reaction of $Si^+(^2P)$ with NH_3

The reaction

$$Si^+ + NH_3 \rightarrow SiNH_2^+ + H \tag{10}$$

is very fast at near thermal energies and its rate coefficient decreases, with increasing KE_{CM} by nearly 2 orders of magnitude, as is shown in Fig. 10. At low energy our data agree well with the value obtained by Wlodek *et al.*[77] Only one product ion of mass 44 has been observed. Assuming the product ion to be the isomer $SiNH_2^+$, the reaction is exoergic by 0.75 eV, the production of the isomer $HSiNH^+$ would be endoergic by 1.57 eV, and is not possible over the whole energy region covered (for energetics of the reaction see data in Table I and for more details concerning energetic of the reaction (10) see discussion in Ref. 77). Figure 11 represents a log–log plot of the function $((\beta\cdot k_0)/(k)-1)$ vs KE_{CM}. Note the extraordinary linearity of the plot indicating a very high accuracy of the approximation of the ratio (k_{-1}/k_2) by the power function, as it was discussed in Introduction. The

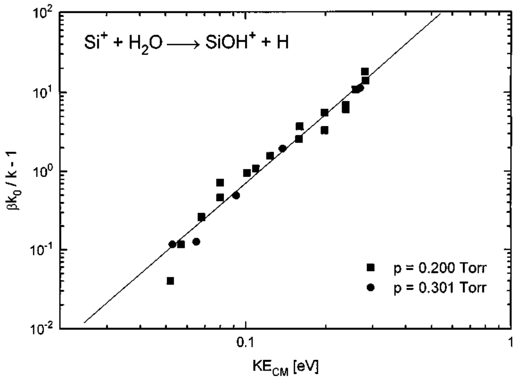

FIG. 9. Plot of $((\beta\cdot k_0)/(k)-1)$ vs KE_{CM} of the reaction rate coefficient for the reaction of $Si^+(^2P)$ with H_2O. Solid straight line is the best apparent linear fit. Different pressures are indicated by different symbols.

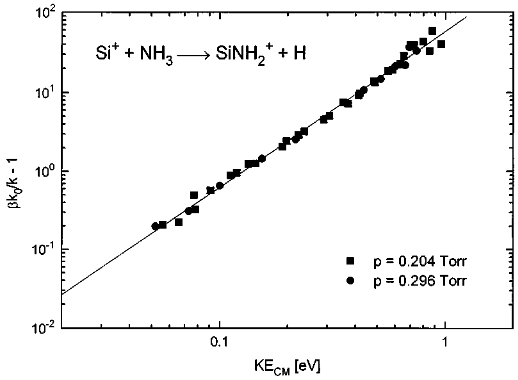

FIG. 11. Plot of $((\beta\cdot k_0)/(k)-1)$ vs KE_{CM} of the reaction rate coefficient of the reaction of $Si^+(^2P)$ with NH_3. Solid straight line indicates the best apparent linear fit. Different pressures are indicated by different symbols.

data in Fig. 11 were fitted by the function given in Eq. (4), parameters m and KE_{CM1} of the fit are listed in Table I.

IV. CONCLUDING REMARKS

We have investigated the dependence of the reaction rate coefficients k on the center-of-mass interaction energy KE_{CM} for several reactions which proceed at near collisional rate (see Table I for k_{10}/k_{CL}) at low KE_{CM} (near thermal collision energies) and for which the reaction rate coefficients decrease quite rapidly with increasing KE_{CM}. We showed that for low KE_{CM} the energy dependence of all studied reactions can be expressed by a power function of the type

$$k \propto k_{C0} \frac{1}{1+(KE_{CM}/KE_{CM1})^m}.$$

These results can be interpreted on the assumption that the reactions are proceeding via formation of long lived intermediate complexes, and in such cases the overall reaction rate coefficients are governed by the ratio k_{-1}/k_2 [see Eq. (2)] of the unimolecular reaction rate coefficient for decomposition of the complex to the reactants (k_{-1}) and the rate coefficient of the forward reaction (k_2). By analogy with ideas used in the interpretation of energy dependencies of the reaction rate coefficients of the three body association processes it was postulated that the ratio $k_{-1}/k_2 \propto (KE_{CM}/KE_{CM1})^m$. Using this assumption an analytical function for energy dependences of the reaction rate coefficients of the studied reactions was derived [see Eqs. (3), (4), and (5)]. The high accuracy of the fits supports our assumption about the nature of the reaction processes.

All four reactions are exoergic (i.e., $\Delta H<0$) but not strongly and the entropy changes in these reactions are negative (i.e., $\Delta S<0$). With increasing KE_{CM} (temperature) in these reactions $T \cdot \Delta S$ becomes increasingly negative, thus the free energy change $\Delta G = \Delta H - T \cdot \Delta S$ becomes positive and therefore unimolecular decomposition back to reactants is favored. The parameter KE_{CM1}, characterizing the energy where the negative energy dependence of the reaction rate coefficient starts, may well coincide with the energy at which ΔG becomes positive.

It is surprising that the ratio k_{-1}/k_2 for all reactions studied shows such a clear "power law" variation with KE_{CM}; this underlines the similarity between the mechanism of the studied reactions and three body association reactions. That similarity, we expect, confirms that the studied reactions proceed via formation of long lived complexes and the lifetime of these complexes determines the kinetics of these reactions.

The linearity of the $\log(k_{-1}/k_2)$ vs $\log(KE_{CM})$ plots (see Figs. 7, 9, and 11) is worthy of theoretical investigations.

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